

The University of Chicago

REACTIONS OF ATOMS AND FREE RADICALS IN
SOLUTION; THE METHYL FREE RADICAL AS
A TOOL FOR ORGANIC SYNTHESSES; THE REL-
ATIVE REACTIVITIES OF SOME LOW MOLEC-
ULAR WEIGHT ALIPHATIC FREE RADICALS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1945

By
HENRY CECIL McBAY

CHICAGO, ILLINOIS
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The writer wishes here to express his sincere thanks to Professor M. S. Kharasch for his patient and skillful guidance throughout this investigation. To Dr. W. H. Urry he is likewise grateful for his interest and many valuable suggestions.

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INTRODUCTION

The term "radical" in the chemical literature goes back as far as the "Method of Chemical Nomenclature," published in 1787 by Lavoisier, Guyton de Morveau and de Fourcroy. These authors considered the molecules of organic compounds to be composed of one or more radicals attached to electronegative oxygen atoms. The first experimental evidence for radicals in chemistry was probably that published by Gay-Lussac in his "Recherches sur L'acide Prussique"¹ in 1815. Gay-Lussac, finding that a group composed of one atom of carbon and one atom of nitrogen seemed to function as a unit throughout a number of reactions, called this group, (CN), "le radical prussique." Indeed, when he prepared cyanogen, (CN)₂, which contained the same percentages of carbon and of nitrogen as those calculated for his "radical," he thought he had isolated the first free radical ever obtained.

As early as 1825 Berzelius² conceived of radicals and in the fifth edition of his "Lehrbuch der Chemie" he describes ammonium, (NH₄), as a compound radical which possesses the properties of an alkali metal. "The hypothesis that the reactions of many organic compounds are the reactions of the radicals, or compound elements, whereof they are supposed to be constituted, was greatly advanced and brought prominently into the daily mental lives of chemists by the researches on the radical of benzoic acid by Wohler³

¹Gay-Lussac, Ann. Chim. Phys., 95, 156 (1815).

²Berzelius, "Lehrbuch der Chemie," 5th Edition, Arnold, Dresden und Leipzig, 1843-1848, Vol. I p. 172, Vol. II p. 103.

³Wohler and Liebig, Ann. Chem., 3, 249 (1832).

and Liebig published in 1832."⁴ This early popularity of the radical theory was, however, short-lived. In 1834, Dumas⁵ began his classical studies of the substitution of chlorine in acetic acid. This work, supported by that of Laurent and Gerhardt, firmly established the theory of substitution and overthrew the original idea that a radical is an unchangeable unit in all organic compounds. Laurent,⁶ however, attempted to reconcile the notion of radicals with the theory of substitution by proposing that there are "fundamental radicals" and "derived radicals." A derived radical he regarded as one in which one or more of the hydrogen atoms in the fundamental radical is replaced by chlorine, bromine, or similar atoms. He pointed out that a derived radical gives to the compound in which it occurs essentially the same properties as those given by the corresponding fundamental radical.

The radical theory, thus reinstated, soon received new impetus from the classical studies of Bunsen,⁷ Kolbe,⁸ and Frankland.⁹ By treating dimethyl-chloroarsine, $(\text{CH}_3)_2\text{AsCl}$, with zinc, Bunsen⁷ prepared cacodyl, $(\text{CH}_3)_2\text{As}-\text{As}(\text{CH}_3)_2$, which he at first thought to be a free radical. He soon realized this compound was a dimer, but chemists still considered the possibility of isolating free radicals. Kolbe⁸ suggested that, during the electrolysis of the salts of organic acids, free radicals are

⁴Pattison Muir, "History of Chemical Theories," John Wiley and Sons, New York, 1906, Chap. 9, p. 241.

⁵Dumas, Ann. Chim. Phys., (2), 56, 113 (1834).
Compt. Rend., 10, 149 (1840); 8, 609 (1839).

⁶Laurent, Ann. Chim. Phys., (2), 60, 220 (1835); (2), 63, pp. 42 and 208 (1838).

⁷Bunsen, Ann. Chem. Pharm., 31, 175 (1839); 37, 1 (1841); 42, 14 (1842); 46, 1 (1843).

⁸Kolbe, Ann. Chem., 69, 258 (1849).

⁹Frankland, Ann. Chem., 71, 171-213 (1849); 74, 63 (1850).

formed at the anode where carbon dioxide is evolved; however, he was unable to isolate free radicals from the products thus formed. Frankland,⁹ following the idea of Bunsen, treated alkyl halides with zinc in sealed tubes; but he, like his predecessors, was unable to isolate free radicals from his products.

The experiments cited, together with the theory (then generally believed) that the carbon atom is invariably tetravalent, confirmed most chemists in the conviction that a radical was only a theoretical concept and that such a substance could never be isolated. There were, however, certain less skeptical workers, among whom was J. U. Nef¹⁰ of the University of Chicago.

A free radical may be defined as an electrically neutral molecule which contains at least one unpaired electron. The best test for the presence of such free radicals is the paramagnetic susceptibility of the compound under investigation. Early in the nineteenth century, Gomberg¹¹ successfully demonstrated that solutions of hexa-arylethanes contain small amounts of triarylmethyl free radicals. Schlenk¹² later prepared hexa-p-biphenylethane which in dilute solution dissociates completely into tri-p-biphenylmethyl free radicals. Free radicals of this type have since been extensively studied, and have been shown to have comparatively long lives. Their properties have been well established. The first purely aliphatic free radical was probably obtained by Frankland⁹ as early as 1850. He, however, failed to realize the full significance of his experiments, doubtless because of the very short life of the free radicals formed in his reactions.

¹⁰See a series of papers by Nef in (Liebig's) Ann. Chem., (1892-1904).

¹¹Gomberg, J. Am. Chem. Soc., 22, 757 (1900).

¹²Schlenk, Weickel, and Herzenstein, Ann. Chem., 372, 1 (1909).

During the past two decades, an increasing amount of attention has been devoted to the study of free radicals of short life. Paneth¹³ and Rice¹⁴ have made exhaustive studies of aliphatic free radicals in the gas phase. This work is important on its own account, but the results obtained show that free radicals in the gas phase probably cannot be developed into useful tools for organic syntheses. On the other hand, even the small amount of work which has been done on the reactions of short-lived aliphatic free radicals in solution^{15,16,17} indicates that such free radicals are extremely promising synthetic tools. Gladstone,¹⁶ and Jensen,¹⁷ under the direction of Kharasch, have already devised a number of synthetic methods involving the use of these short-lived free radicals. The purpose of the present investigation has been to pursue the study of organic free radicals, particularly aliphatic free radicals, in solution, and to develop further their use in organic syntheses.

Before such theories as those of resonance¹⁸ and electronegativity¹⁹ had been advanced, most chemists believed that a free radical must necessarily possess energy enough to make it react instantly with the first molecule with which it collided. However, the above-mentioned work^{11,12,15} on free radicals in solution has shown that these radicals not only differ widely in their half-life periods, but also in their relative reactivities. The long-lived hexaarylethanes, which dissociate into triarylmethyl

¹³Paneth, Ber., 62B, 1335 (1929); 64, 2702 (1931).
Z. Phys. Chem., 7B, 155 (1930).

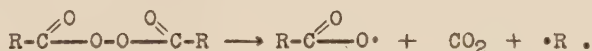
Paneth and Lautsch, Nature, 125, 564 (1930).

¹⁴Rice and Rice, "Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Maryland, 1935.

¹⁵Hey and Waters, Chem. Reviews, 21, 169 (1937).
Ann. Reports Chem. Soc., 275-90 (1940).

free radicals in solution, can be recrystallized from most organic solvents, whereas many of the short-lived aliphatic free radicals as well as the phenyl free radical react with many of these solvents.^{15,16,17} Evidence will be presented herein to support the belief that aliphatic free radicals, despite their high reactivity, must undergo many unsuccessful collisions before they ultimately react. It will furthermore be shown that, even among the aliphatic free radicals, there are wide differences in reactivity. In fact, such free radicals may be arranged in a series with respect to their relative reactivities in much the same way as ordinary radicals may be arranged with respect to their varying degrees of electronegativity.¹⁹

Organic free radicals may be generated in solution by several different methods.¹⁵ Only one of these methods, namely the thermal decomposition of diacyl peroxides, was used in the work here reported. The first step in the proposed¹⁵ mechanism for this decomposition is



Results comparable to some of those presented here have, however, been obtained by Kharasch and Urry²⁰ who generated free radicals by the action of cobaltous chloride on mixtures of alkyl halides and alkyl Grignard reagents. The proposed mechanism²⁰ for these

¹⁶Kharasch and Gladstone, J. Am. Chem. Soc., **65**, 15 (1943).

¹⁷Kharasch, Jensen, and Urry, Unpublished results.

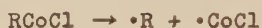
¹⁸Wheland, "The Theory of Resonance," John Wiley and Sons, New York, 1944.

¹⁹Kharasch and Reinmuth, J. Chem. Ed., **5**, 404-18 (1928); **8**, 1703-48 (1931).

Kharasch, Reinmuth, and Mayo, J. Chem. Ed., **11**, 82-96 (1934); **13**, 7-19 (1936).

²⁰Kharasch and Urry, Unpublished results.

reactions is:

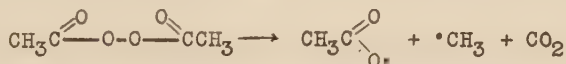


The work herein reported has been divided into two parts. The first part contains a detailed treatment of the reactions which occur when diacetyl peroxide is decomposed in various organic solvents. Here also is included the report of an investigation of the fate of the free acetoxy radical, $(\text{CH}_3\text{C}^{\text{O}}\text{O}\cdot)$, which is one of the proposed products of these decompositions. The second part is a comparative study of the results obtained when various aliphatic diacyl peroxides are decomposed successively in the same solvents.

THEORETICAL PART I

THE METHYL FREE RADICAL AS A TOOL FOR ORGANIC SYNTHESSES

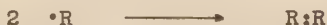
The general procedure for conducting the reactions here described was to dissolve pure diacetyl peroxide (free from ether and water) in the desired solvent, and to add this solution dropwise beneath the surface of an excess of the same solvent heated to a temperature (usually above 95°C.) sufficiently high to decompose the peroxide. The "initial" free methyl radicals thus generated¹ by the reaction



in turn react with the solvent as follows:



where U is some univalent atom and R is the residue of the solvent molecule. Previous work² in this laboratory has indicated that the "residual" free radical $\cdot\text{R}$ dimerizes.



The extraction of an atom from a molecule of the solvent is not a random process; on the contrary, the methyl free radical exhibits a definite selectivity in its cleavage reactions. This pronounced selectivity, first observed by Kharasch and Gladstone,^{2a}

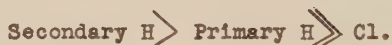
¹Hey and Waters, Chem. Reviews, 21, 169 (1937).

^{2a}Kharasch and Gladstone, J. Am. Chem. Soc., 65, 15 (1943).

^bKharasch, Jensen, and Urry, Unpublished results.

and by Kharasch, Jensen, and Urry,^{2b} has repeatedly been verified in the work reported in this paper. Such selectivity indicates that the methyl free radical does not necessarily react during its first collision. The various activation energies associated with the different atoms of the molecule attacked seem largely to direct the course of the reaction. It is exceedingly improbable that every free methyl radical strikes the right point in its first collision. Probably many unsuccessful collisions occur before any reaction takes place.

Jensen³ states that the methyl free radical attacks the atoms of the solvent molecules in the following order of preference:



This generalization holds for all cases studied thus far, but it is nevertheless to be accepted with some reservation. There may well exist molecules containing both hydrogen atoms and chlorine atoms in which at least one chlorine atom is more easily activated than any hydrogen atom present. From such a molecule the more easily extracted chlorine atom would almost certainly be selectively removed by the free methyl radical. The question thus raised deserves further investigation.

When the methyl free radical cleaves an atom from a molecule of the solvent,



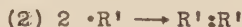
there is left behind another free radical, fate of which determines the final products obtained in these reactions. This

³Jensen, Doctor's Thesis, Department of Chemistry, University of Chicago, 1944.

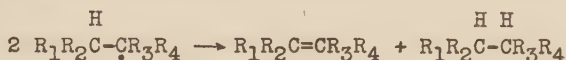
"residual" radical $\cdot R$ may react in various ways of which the following are the most probable:*

A) It may rearrange: $\cdot R \longrightarrow \cdot R'$

B) Either $\cdot R$ or $\cdot R'$ may dimerize:



C) If the free radical $\cdot R$ or $\cdot R'$ is of the form, $R_1R_2\overset{H}{\underset{|}{C}}\cdot CR_3R_4$, it may then disproportionate according to the reaction



(R_1, R_2, R_3 , or R_4 may be hydrogen atoms, alkyl or aryl groups, or portions of a ring structure).

The solvents chosen for tests in this work were the following:

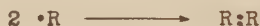
- | | |
|--|------------------------------|
| 1. Trichloroacetyl Chloride | 6. Isopropylbenzene |
| 2. Methyl Dichloroacetate | 7. p-Methoxy-n-propylbenzene |
| 3. Dimethyl Succinate and Methyl Acetate | 8. Trimethyl Acetic Acid |
| 4. Methyl Acetoacetate | 9. Ketones |
| 5. Ethylbenzene | Methyl Ethyl Ketone |
| | Acetophenone |
| | Propiophenone |
| | Phenyl Isopropyl Ketone |

In every instance where definite products were isolated from the reaction mixture, these products indicated that the "residual" free radicals ($\cdot R$) had undergone dimerization. When any one of the three aromatic ketones, acetophenone, propiophenone, or phenyl isopropyl ketone, was used as a solvent, no definite condensation

*In view of the highly selective action of free methyl radicals in solution, it is superfluous to consider the possibility that the residual radicals may react with the molecules of the solvent. If they did so they would almost certainly cleave from the solvent molecules the atom analogous to the one originally extracted by the methyl free radical. The reaction would therefore be $\cdot R + UR \longrightarrow UR + \cdot R$ where the reactants and the products are identical.

products were isolated. It should be remembered, however, that the solvents were so chosen that dimerization was the expected course of the reactions of the residual radicals. There are other aliphatic free radicals which do not as a rule dimerize.

The reaction



does not account for all the products obtained by the generation of methyl free radicals in the solvents listed above. However, this is not surprising, for, if the dimer, $R:R$, contains a univalent atom U' which yields to cleavage about as easily as does the atom U in the original solvent molecule UR ; then the free methyl radical should cleave this reactive atom U' from the dimer with about the same ease as it cleaves the atom U from UR .



The resulting free radical, $\cdot R:R$, may be called a "residual free radical of the second order." Such a free radical may either combine with a residual free radical of the first order,



or it may dimerize



The process just outlined need not stop at the point indicated. Either $R:R:R$ or $R:R:R:R$ may contain a highly reactive univalent atom. If such is the fact, the methyl free radicals tend to form from $R:R:R$ or from $R:R:R:R$ free radicals of the third order, etc. This process might conceivably go on indefinitely.

When methyl free radicals are generated in any one of the solvents listed above, one might expect to obtain varying amounts

of material of higher molecular weight. The amount of such condensate formed should depend upon the concentrations of the various free radicals present at any given moment. This concentration in turn depends upon the relative reactivities of the univalent atoms in the various molecules present in each of the reaction mixtures. When the conditions conducive to the formation of these residual free radicals of higher orders are fulfilled, the tendency toward formation of heavy residues limits the usefulness of the suggested method of synthesis. This tendency can be partially controlled by using only small amounts of peroxide and large amounts of solvent in any one experiment. By this means the concentration of the residual free radicals of higher orders is kept low. When particular cases are discussed, it will be seen that, although the amounts of heavy condensates obtained are generally small, they throw considerable light on the probable course of reactions in which they are formed.

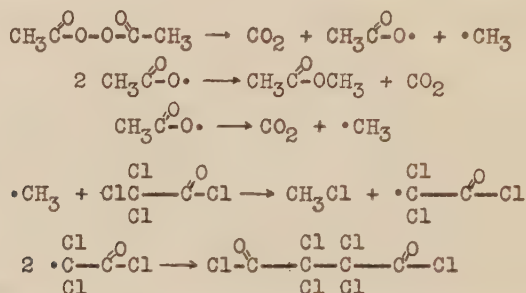
1. Trichloro-acetyl Chloride. The work here reported makes available a unique method for synthesizing some derivatives of tetrachlorosuccinic acid, the preparation and properties of which have been the subject of controversy.⁴ Indeed, some⁵ previous workers have maintained that, by direct methods, it is impossible to replace all four of the secondary hydrogen atoms in succinic acid or its derivatives by chlorine. It is certainly true that mono, di, and tri-chloro derivatives of this acid have been clearly characterized, but no tetrachloro derivative has heretofore been definitely identified.

⁴Fehling, "Neues Handwörterbuch der Chemie," F. Viewig und Sohn, Braunschweig, 1875, Vol. II, pp. 20-21.

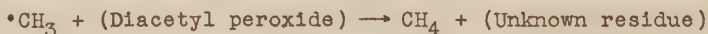
Cahours, Ann. Chim. Phys., (3), 9, pp. 206 ff. (1843).

⁵Malaguiti, Ann. Chem., (3), 16, 67-75 (1846).

In the attempt to prepare such tetrachloro derivatives, methyl free radicals were generated in trichloro-acetyl chloride; by this means 80% yields of tetrachloro succinyl chloride were obtained.



It is important that, in this reaction, a large quantity of methane gas was obtained in addition to the expected methyl chloride. The formation of methane was at first attributed to the presence of unremoved ether in the peroxide; but methane was still obtained in large quantities even after extreme care had been exercised in removing all traces of ether and moisture from the reactants. These findings strongly support the hypothesis that the chlorine atoms in trichloroacetyl chloride are relatively unreactive; hence, the methyl free radicals tend to attack the molecules of their mother substance, diacetyl peroxide, from which the secondary hydrogen atoms adjacent to the carbonyl groups are much more easily extracted.

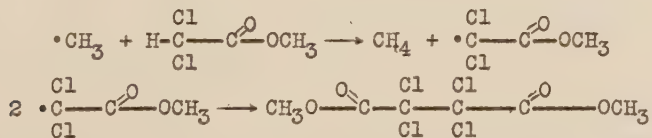


The gummy residue obtained among the reaction products probably resulted from the polymerization of the unsaturated fragments left when methyl free radicals attack the peroxide molecules. The methane found was probably not formed by the action of methyl free radicals on traces of ethyl ether possibly present, for the

amount of methane found was too great to have originated from any traces of impurities in the carefully purified reactants. Moreover, other experiments have shown that when free radicals attack ethyl ether, acetaldehyde is formed, whereas no acetaldehyde was found among the reaction products here obtained. The tendency to attack the easily extracted hydrogen atoms of substances present in very low concentration rather than the chlorine atoms of trichloroacetyl chloride, present in high concentration, is a striking example of the selective action of the methyl free radical.

Tetrachlorosuccinyl chloride is hydrolyzed only very slowly, even when warmed with dilute alkali. This fact is not surprising if the possible steric hindrance caused by the four alpha chlorine atoms is considered. This hitherto unknown acid chloride was characterized by its molecular weight, its saponification equivalent, and its chlorine content. The corresponding di-N-methyl anilide was prepared, and its nitrogen and chlorine contents agreed with the calculated values. The tetrachlorosuccinyl chloride was also converted by alcoholysis into the dimethyl ester which proved to be identical with the material described in the next section.

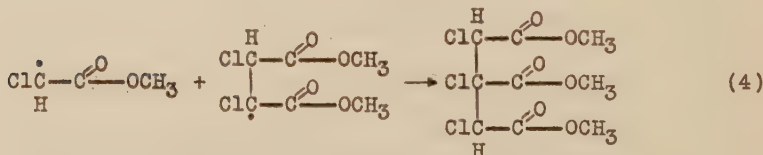
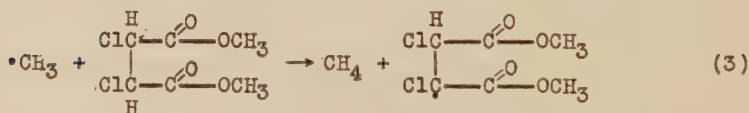
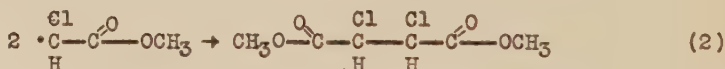
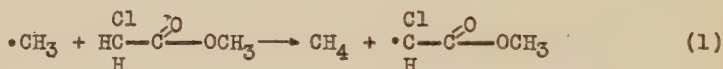
2. Methyl Dichloroacetate. When diacetyl peroxide was decomposed in methyl dichloroacetate, a 70% yield of dimethyl tetrachlorosuccinate was obtained.



This compound had the same boiling point and index of refraction as the material mentioned above. Its chlorine content checked with the calculated value. It was converted by catalytic

hydrogenation to dimethyl succinate which was identified by its boiling point and refractive index. The dimethyl succinate was in turn converted to succinamide which failed to depress the melting point of a known sample of that substance. The results given in this and the preceding section confirm one another. There can therefore be no doubt that derivatives of tetrachlorosuccinic acid can be prepared provided a proper synthetic method is used.

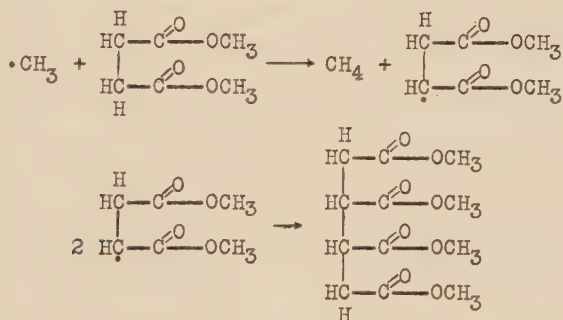
3. Dimethyl Succinate and Methyl Acetate. Diacetyl peroxide was decomposed in methyl chloroacetate by Jensen.³ He reported a small amount of symmetrical trimethyl trichlorotricarballylate in addition to the main product, dimethyl α, α' -dichlorosuccinate. He states that the products were probably formed by the pairing of residual free radicals, as indicated by the following equations.



During the reaction, as carried out by Jensen, the concentration of the free radicals must have been very small owing to the large excess of solvent (methyl chloroacetate) used. Thus it seemed probable that good yields of the tricarballylic ester

itself might be obtained by generating methyl free radicals in a mixture of methyl acetate and dimethyl succinate. Hence, diacetyl peroxide was thermally decomposed first in pure dimethyl succinate and then in a mixture of dimethyl succinate and methyl acetate.

When pure dimethyl succinate was used as a solvent, an almost quantitative yield of the tetramethyl ester of butane 1,2,3,4-tetracarboxylic acid was obtained. The reaction is evidently a straight-forward dimerization.



The compound obtained should exist in stereoisomeric forms. A small amount of a higher-melting (134°C.) form, sparingly soluble in ethyl ether was isolated; but by far the greater portion (98%) of the material obtained was a lower-melting (73°C.) form, much more soluble in ether. The molecular weights of both forms as well as their carbon and hydrogen contents checked the calculated values; their saponification equivalents were likewise correct.

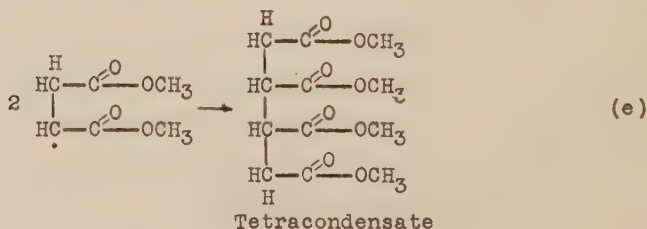
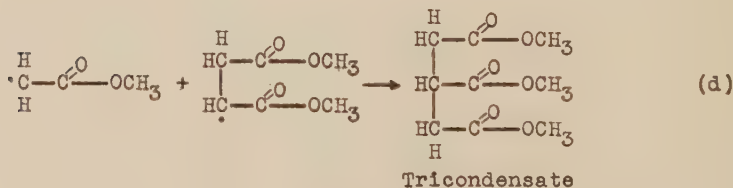
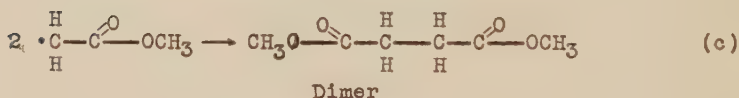
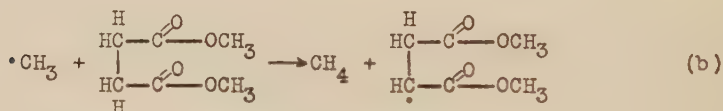
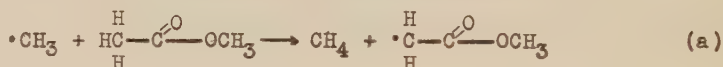
The tetra-amides derived from both the high and the low-melting forms of the tetramer were prepared, and their nitrogen contents checked with the calculated value.

The corresponding tetracarboxylic acids have previously been prepared⁶ from ethyl aconitate and the sodium salt of malonic ester by the Claisen condensation. The melting points of the two

⁶Auwers, Ber., **26**, 364 (1893); **27**, 1114-5 (1894).

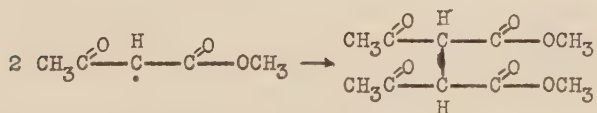
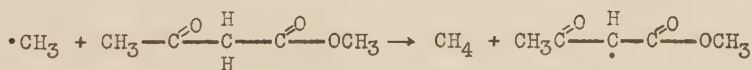
forms of this acid reported by Auwers⁶ are essentially the same as those reported here. However, the melting point of one of Auwers' tetramethyl esters is appreciably lower than that of the corresponding ester here obtained. Such an acid would probably be difficult completely to esterify because of steric hindrance. Auwers prepared his esters by esterification of the parent acids and was probably unsuccessful in completely esterifying one of them. In the present work the esters were prepared directly, hence incomplete esterification was impossible.

Methyl free radicals were generated in a mixture of dimethyl succinate and methyl acetate (2 molar equivalents of the former to 3 molar equivalents of the latter). The following scheme of reactions represents the theoretical probabilities.

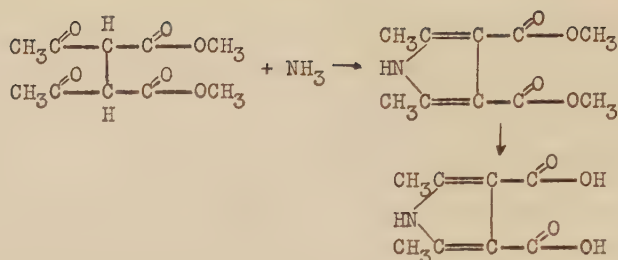


The formation of the dimer (dimethyl succinate) according to reaction (c) would be difficult to demonstrate because this substance is one of the solvents. The dimer and the tricondensate are well-known compounds, and the tetracondensate (e) had been fully characterized (see preceding paragraph) before the experiments in the mixed solvent were undertaken. No detectable amount of tricondensate (d) was formed in the mixed solvent. The yield of tetracondensate (e) was, however, almost quantitative. The two forms of the tetracarboxylic ester were obtained in approximately the ratio found when pure dimethyl succinate was used as the solvent (see page 15). The formation of much tetracondensate in the mixed solvent (containing 3 molar equivalents of methyl acetate to 2 molar equivalents of dimethyl succinate) is highly significant. This result illustrates the strong tendency of free methyl radicals (at least when generated under conditions similar to those described in this paper) to extract secondary hydrogen atoms rather than primary hydrogen atoms from solvent molecules.

4. Methyl Acetoacetate. When diacetyl peroxide was decomposed in methyl acetoacetate, a 70% yield of dimethyl a,a'-diaceto-succinate was obtained.

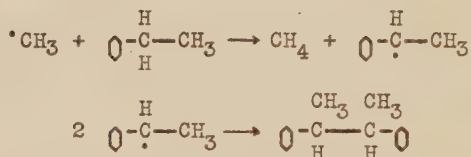


The white crystalline product was converted by treatment with ammonium hydroxide and subsequent saponification to 2,5 dimethyl pyrrole-3,4-dicarboxylic acid.



The pyrrole derivative thus obtained melted at 247-50°C. The melting point recorded in the literature⁷ is 250-1°C.

5. Ethylbenzene. When diacetyl peroxide was decomposed in ethylbenzene, equimolar quantities of the meso and racemic forms of 2,3-diphenylbutane were obtained. The total yield was 64%.



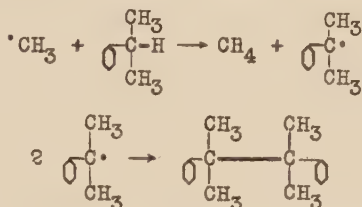
The physical constants of these compounds were identical with those recorded in the literature.⁸ The reaction gave, in addition, twenty grams (20 g.) of a yellowish glassy material with a molecular weight of 425. The presence of this high-molecular-weight fraction is easily explained by the assumption that free methyl radicals extract the tertiary hydrogen atoms from the 2,3-diphenylbutane more easily than they cleave the secondary hydrogen atoms from ethylbenzene itself. This behavior is exactly in line with the general ideas already developed (see page 10). It follows from these ideas that, if all the univalent atoms in the molecules of the dimer are much more difficult to extract than any univalent

⁷Knorr, Ber., 18, 302 (1885).

⁸Conant and Blatt, J. Am. Chem. Soc., 50, 555 (1928).
Ott, Ber., 61, 2139 (1928).

atom in the molecules of the original solvent, the final product should be pure dimer. No higher condensates should appear. The solvent next discussed fulfills the stated conditions and reacts exactly as predicted.

6. Isopropylbenzene. When diacetyl peroxide is decomposed in isopropylbenzene, the yield of 2,3-diphenyl 2,3-dimethylbutane (m.p. 115°C.)⁹ is practically quantitative.



Isopropylbenzene contains a hydrogen atom which is easily extracted both because it is tertiary and because the carbon to which it is attached is adjacent to a benzene ring. On the other hand, all the aliphatic hydrogen atoms in 2,3-diphenyl 2,3-dimethylbutane are primary and therefore much more difficult to extract. Hence, in the reaction in question, no higher condensate is formed.

7. p-Methoxy-n-Propylbenzene. The method of synthesis already described was used to prepare hexestrol dimethyl ether from p-methoxy-n-propylbenzene. Equimolar quantities of the racemic and meso forms of hexestrol dimethyl ether were obtained. The total yield was 80%.



⁹Klages, Ber., **35**, 2638 (1902).



The meso form melted at 142°C . which agrees with the recorded¹⁰ value. Docken and Spielman obtained the racemic form, but probably never in a pure state. Their product boiled over a wide range ($155\text{--}90^{\circ}\text{C}/0.2\text{ mm.}$), and deposited crystals (m.p. 53°C .) when allowed to stand. The liquid form (presumably racemic) obtained here boiled sharply ($172\text{--}5^{\circ}\text{C}/2\text{ mm.}$) and deposited no crystals even when allowed to stand for a year. A glassy material (9.5 g.) with a molecular weight of 460 was formed in the reaction in addition to the dimerized products mentioned. This molecular weight is close to that of a tricondensate (446). The dimer has two tertiary hydrogen atoms adjacent to the benzene rings. These are more easily extracted than the secondary hydrogen atoms in the solvent molecule; hence the tendency to form condensates of higher molecular weight.

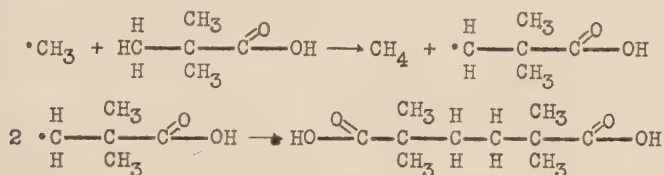
Urry¹¹ has synthesized all the products described in Sections 5, 6, and 7. He, however, formed his methyl free radicals by catalyzed Grignard reactions. Because the free methyl radicals tended to attack the small amounts of ether necessary for the Grignard reactions, his yields were much lower than those recorded here. Despite these low yields, his results furnish additional evidence in favor of the free radical mechanisms proposed for both these types of reactions.

8. Trimethyl Acetic Acid. When diacetyl peroxide was decomposed in trimethyl acetic acid (a solvent molecule in which

¹⁰Docken and Spielman, J. Am. Chem. Soc., **62**, 2163 (1940).

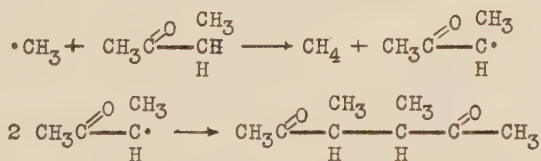
¹¹Kharasch and Urry, Unpublished results.

all the hydrogen atoms are primary), a 71% yield of a white crystalline product (m.p. 187°C. unc.) was obtained.



The melting point of a,a,a'-tetramethyl adipic acid, as reported in the literature,¹² is 191°C. Here again there was a small amount of glassy material supposedly formed by the action of the methyl free radical on the dimerized product. The relatively low yield (71%) of the dimer may be further attributed to the fact that trimethyl acetic acid contains only primary hydrogen atoms which are extracted with difficulty by the methyl free radical. Hence this radical tends to attack the dimer, traces of moisture, or even the peroxide itself, since all three of these substances contain more easily extractable hydrogen atoms.

9. Ketones. Diacetyl peroxide was decomposed in various ketones. When ethyl methyl ketone (which is purely aliphatic) was used as a solvent, an 87% yield of the corresponding dimer, 3,4-dimethylacetylonyl acetone, was obtained.



The product thus formed was identified as follows. Like most aliphatic 1,4-diketones it colors the skin red. It condenses with phenylhydrazine to form a compound melting at 127°C. The melting point of 2,3,4,5-tetramethyl-N-phenyl pyridazine as given

¹²Farmer and Kracovski, J. Chem. Soc., 2318-23 (1936).

in the literature¹³ is 130°C. The compound here formed has a nitrogen content corresponding to that of this pyridazine. Furthermore, the supposed 1,4-diketone, when treated with ammonia, yielded the known¹³ 2,3,4,5-tetramethyl pyrrole (m.p. 109-10°C.). Finally, the diketone, when oxidized with sodium hypobromite, gave a,a'-dimethylsuccinic acid. Along with the diketone there was obtained 4.3 grams of a higher boiling oil probably formed by the attack of the methyl free radical on the dimerized product.

The products and yields obtained from the reactions in Solvents 1-9 are listed in the table on the following pages.

When diacetyl peroxide was decomposed in acetophenone, propiophenone, or phenyl-isopropyl ketone, the only non-volatile products obtained were resins which resisted all attempts to purify them. Later work has shown that this unexpected behavior of these solvent molecules is due to the fact that each one of them contains a phenyl group adjacent to the carbonyl group. No further explanation of this behavior is possible at present.

When diacetyl peroxide is decomposed in various solvents, methane, carbon dioxide, and methyl acetate are always formed. A few words to explain the relative amounts of these products (see Table 1) are in order. There are three facts to be explained.

(a) The yield of methane accounts for about 63% mole per cent of the peroxide used.

(b) The numbers of the moles of methane and of carbon dioxide formed are both greater than the number of moles of peroxide used.

(c) The number of moles of carbon dioxide is about equal to the sum of the number of moles of methane and the number of

¹³Demetre-Vladesco, Bull. Soc. Chim., (Paris) (3), 4, 89 (1891).

Ciamician, Ber., 45, 1542 (1912).

TABLE 1

Decomposition of Diacetyl Peroxide in

	Trichloro- acetyl chloride	Methyl dichloro- acetate	Dimethyl succinate at 110°C.	Dimethyl succinate at 160°C.
Reagents (moles)				
Acetyl peroxide	.369	.412	.208	.355
Solvent used	1.30	2.00	1.67	1.90
Solvent recovered		1.32	1.38	1.60
Products (moles)				
Methane	.348	.51	.257	.447
Carbon dioxide	.51	.670	.297	.581
Methyl acetate		.10	.038	.081
Methyl chloride	.05			
Acetyl chloride	.09			
Tetrachloro succinyl chloride	.19			
Dimethyl tetrachloro- succinate		.17		
1,2,3,4- Tetra methyl- carbomethoxy- butane			.103 ^a	.146 ^a
Hydrogen chloride	.07	.01		

^a02% high-melting (134°C.) form; 98% low-melting (73°C.) form.

TABLE 1--Continued

Decomposition of Diacetyl Peroxide in					
	A Mixture of		Methyl aceto- acetate	Ethyl methyl ketone	Trimethyl acetic acid
	Dimethyl succinate	Methyl acetate			
Reagents (moles)					
Diacetyl peroxide	0.351		0.224	0.516	0.52
Solvent used	1.28	1.80	1.10	4.00	3.51
Solvent reclaimed	0.90	1.80	.85	3.30	3.06
Products (moles)					
Methane	0.364		.282	.62	.60
Carbon dioxide	.374		.370	.79	.88
Methyl acetate	-----		.05	.08	.08
1,2,3,4- Tetra methyl carbomethoxy butane	.138 ^a				
Dimethyl diaceto- succinate			.10		
2,3-dimethyl acetyl acetone				.269	
a,a,a',a'- tetramethyl adipic acid					.214
Unidentified residues				4.3 grams	6.3 grams
Acetic acid					.07

^a03% high-melting (134°C.) form; 97% low-melting (73°C.) form.

TABLE 1--Continued

Decomposition of Diacetyl Peroxide in			
	Isopropyl- benzene (moles)	Ethyl- benzene (moles)	p-methoxy- n-propylbenzene (moles)
Reagents			
Acetyl peroxide	0.436	0.56	0.506
Solvent used	2.00	2.33	2.60
Solvent recovered	1.43	1.69	2.16
Products			
Methane	0.56	0.61	0.57
Carbon dioxide	0.74	0.90	0.745
Methyl acetate	0.06	0.09	0.05
Dimer and higher polymers	0.27 ^a	0.295 ^b	0.23 ^c

^aPure 2,3-dimethyl-2,3-diphenylbutane.

^bMeso 2,3-diphenylbutane (0.09 mole), racemic 2,3-diphenylbutane (0.09 mole), and 18.5 g. of tetramer.

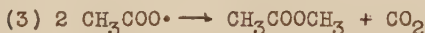
^cCrystalline form of hexestrol dimethyl ether (0.07 mole), liquid form of hexestrol dimethyl ether (0.07 mole), and 9.5 g. of trimer.

moles of methyl acetate.

These observations are readily explained if the following series of steps is assumed for the decomposition of the peroxide.



The acetoxy free radical thus formed may react in a number of different ways.



The formation of more than one mole of methane and of carbon dioxide per mole of peroxide is readily explained by reactions (1) and (2). The excess of carbon dioxide over methane may be attributed to the occurrence of reactions (3) and (4). This explanation further agrees with the fact that the excess of carbon dioxide (in moles) is very nearly equivalent to the number of moles of methyl acetate. The formation of methyl acetate by the direct combination of methyl and acetoxy free radicals seems rather unlikely. Another possible mechanism for the formation of methyl acetate is:



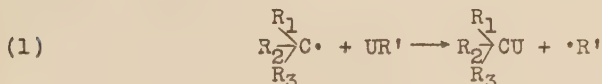
Diacetyl peroxide was decomposed in the same solvent (dimethyl succinate) at two different temperatures. It was found (see Table 1, p. 23) that the relative amount of carbon dioxide obtained was appreciably greater at the higher temperature. This indicates that reaction (2) was probably favored at the higher temperature. As yet, however, it is impossible to account for all the free acetoxy radicals.

THEORETICAL PART II

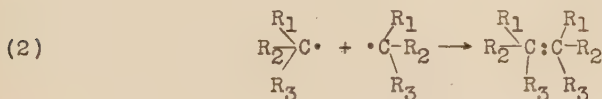
THE RELATIVE REACTIVITIES OF SOME LOW MOLECULAR WEIGHT ALIPHATIC FREE RADICALS

An important part of this study has been the attempt to determine at least qualitatively the relative reactivities of some simple aliphatic free radicals as the length of the carbon chain increases or as the electronegativity of the radical R: (of which the free radical R• is a derivative) decreases.

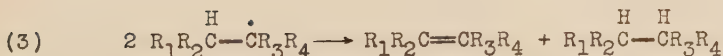
The known important reactions of free alkyl radicals are three in number.



(Extraction of an atom from a solvent molecule)



(Dimerization)



(Disproportionation)

(R₁, R₂, R₃, and R₄ may be either hydrogen atoms or alkyl groups.)

It is believed that the free methyl radical reacts in solution only by cleaving an atom from a neighboring molecule (reaction 1) or by dimerizing to give ethane (reaction 2). The experiments reported in Part I show that this radical frequently reacts according to (1). It is known to dimerize to some extent in the gas phase. The conditions necessary for disproportionation (3)

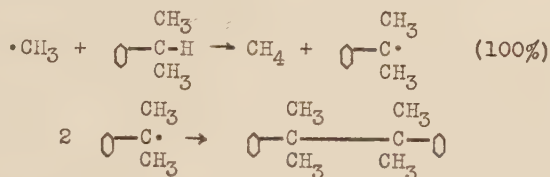
are lacking in the free methyl radical. Many other alkyl free radicals do, however, meet the structural conditions necessary for reaction (3). Some of these are known to disproportionate to some extent in solution.¹

The work of Kharasch, Kane, and Brown² has shown that some free alkyl radicals attack certain solvent molecules which under similar conditions seem less readily accessible to attack by other (apparently less energetic) alkyl free radicals. When the solvent is not attacked by such less energetic free radicals, these radicals must react in some different way, presumably either by dimerization or by disproportionation. Evidence presented in Part I of this paper indicates that the methyl free radical, when generated either in a pure solvent or a mixture of solvents, always follows the course of least resistance by extracting from a solvent molecule that atom which is held by the weakest bond. A free radical which, unlike the methyl free radical, is able to disproportionate as well as to attack the solvent or to dimerize might, when generated in the same solvent, give a lower yield of the product resulting from the cleavage reaction (1) and higher yields of products resulting from disproportionation (3) and/or dimerization (2). The fundamental assumption here is, of course, that the energy barrier for cleavage is greater than that for disproportionation or dimerization. In order to test this idea it was decided to generate methyl ($\cdot\text{CH}_3$), n-propyl ($\text{CH}_3\text{CH}_2\text{CH}_2\cdot$), and t-butyl [$(\text{CH}_3)_3\text{C}\cdot$] free radicals successively in the same solvent and to compare the yields of the products expected from each of the three modes of reaction cited. These

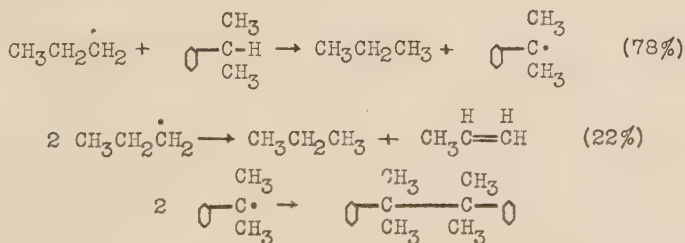
¹Kharasch, Lewis, and Reynolds, J. Am. Chem. Soc., **65**, 493 (1943).

²Kharasch, Kane, and Brown, J. Am. Chem. Soc., **64**, 1621 (1942).

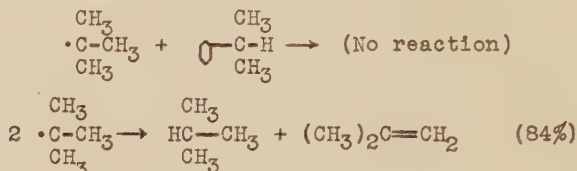
purposes were accomplished by decomposing diacetyl, dibutyryl, and ditrimethylacetyl peroxides successively in isopropylbenzene. This solvent was chosen because its molecule contains a tertiary hydrogen atom adjacent to a benzene ring. This hydrogen atom is easily extracted by free radicals. The methyl free radical cleaves it quantitatively, and 100% yields of 2,3-diphenyl-2,3-dimethylbutane and methane are obtained.



When n-propyl free radicals were generated in the same solvent the yield of the 2,3-diphenyl 2,3-dimethylbutane was only 78%. The gas obtained in this reaction was 90% propane and 10% propylene. This finding indicates that 78% of the free propyl radicals reacted (as did all of the free methyl radicals) by cleaving the tertiary hydrogen atom from isopropylbenzene. The remaining 22% of the propyl free radicals evidently disproportionated to give propylene (11%) and propane (11%). The 78% yield of propane resulting from the cleavage reaction added to the 11% yield of propane from the disproportionation reaction gives 89% as the total yield of propane (90% actually determined by gas analysis).



When tertiary butyl free radicals, $(\text{CH}_3)_3\text{C}\cdot$, were generated in isopropylbenzene no 2,3-diphenyl 2,3-dimethylbutane was obtained. The mixture of gaseous hydrocarbons produced was 58% isobutane and 42% isobutene (by gas analysis). This finding indicates that the tertiary butyl free radical under these conditions reacts largely (84%) by disproportionation.



The reactions just cited were run under identical conditions. The products obtained and the comparative yields of these products indicate that the methyl free radical has the greatest tendency to react by cleavage, that the propyl free radical shows a smaller tendency to react in this way, and that the tertiary butyl free radical shows the least tendency of these three to undergo this reaction. That is to say, these free radicals when arranged with respect to their tendencies to react by cleavage follow this order:



The tendencies of these free radicals to disproportionate into the corresponding paraffins and olefines follow exactly the reverse order. In none of the reactions thus far reported in this work was any dimerization of these initial free radicals observed. The quantitative findings are given in Table 2.

Experiments reported in Part I show that primary hydrogen atoms are less easily cleaved by the methyl free radical than are tertiary hydrogen atoms. It was assumed that these hydrogen atoms would show similar differences in reactivity when attacked

TABLE 2

Radical	Solvent	% Cleavage	% Disproportionation	% Dimerization
Methyl	Cumene	100	0	0
N-propyl	Cumene	78.3	20.0	0
T-butyl	Cumene	0.	84.	0

by heavier alkyl free radicals which (unlike the methyl radical) cannot only dimerize and cleave but also disproportionate. With this idea in mind it became of interest to determine the percentages of the various products obtained when such a heavier alkyl free radical was generated first in a solvent containing tertiary hydrogen atoms and then in a solvent containing only primary hydrogen atoms. For the purposes of this test the free radical chosen was propyl (which had already been shown to disproportionate), and the solvents chosen were isopropylbenzene and trimethylacetic acid. The products obtained when dibutyl peroxide was decomposed in the two solvents just mentioned are given in Table 3. For purposes of comparison the products obtained when diacetyl

TABLE 3

Radical	Solvent	% Cleavage	% Disproportionation	% Dimerization
Methyl	Isopropylbenzene	100	0	0
	Trimethylacetic acid	71	0	0
N-propyl	Isopropylbenzene	78.3	20	0
	Trimethylacetic acid	(0-3.)	20	50

peroxide is decomposed in the same two solvents are included. A complete and detailed description of the isolation and identification of all products implied by this table is given in the Experimental Part.

The first interesting conclusion to be drawn from Table 3 is that isopropylbenzene is more easily attacked by both the methyl and propyl free radicals than is trimethylacetic acid. This finding is in agreement with the assumption made in the previous paragraph. The second conclusion is that each of these solvents is more easily attacked by the methyl than by the propyl free radical. This finding is in agreement with all the results reported in the first section of Part II. The third and most important conclusion is that when the propyl free radical (which can disproportionate) is generated in a solvent difficult to attack, it shows no more tendency to disproportionate than it does when generated in a solvent which is easily attacked. Instead it tends to undergo a reaction one product of which is n-hexane. This type of behavior may well be general for all solvents and for all aliphatic free radicals which can disproportionate, but the evidence at present available is insufficient to establish so wide a generalization.

These results indicate that, by proper choice of a solvent, it is possible to reduce the attack of a free alkyl radical on the solvent in which it is generated, and thus to force that free radical to react (at least in part) in other ways. Seldom do the disproportionation and dimerization products formed under these conditions account for all of the peroxide which reacts. Thus when either the methyl or the propyl free radical is generated in trimethylacetic acid, the sum of all the products found accounts for only 70-75% of the total peroxide consumed. The fate of the

remaining material needs further investigation.

One fact, however, is quite evident from all the studies reported in this paper. In these reactions of aliphatic free radicals in solution two factors are important; namely, the relative reactivity of the initial free radical in question and the comparative strengths of the bonds holding the univalent atoms in the molecules of the solvents in which the initial free radical is generated.

EXPERIMENTAL PART

Reagents

Trichloroacetyl chloride. Prepared from Eastman's pure grade trichloroacetic acid.¹ (b.p. 118°C.; $n_D^{20} = 1.4698$)

Methyl dichloroacetate. Prepared from Eastman's pure grade dichloroacetic acid.² Distillation through a 12-plate column gave a product with b.p. 141°C.; $n_D^{20} = 1.4424$.

Dimethyl succinate. Prepared² from Merck's reagent grade succinic acid. Distillation through a 12-plate column gave a product with b.p. 80°C./11 mm.; $n_D^{20} = 1.4190$.

Methyl acetate. Distillation of Eastman's pure material through a 30-plate column packed with single-turn glass helices gave a product with b.p. 57.5-58°C.; $n_D^{20} = 1.3600$.

Methyl acetoacetate. Distillation of the ordinary reagent through a 12-plate column gave a product with b.p. 71-2°C./22 mm.; $n_D^{20} = 1.4230$.

Ethyl methyl ketone. Distillation of Eastman's pure material through a 12-plate column packed with glass helices gave a product with b.p. 78°C.; $n_D^{20} = 1.3799$.

Trimethyl acetic acid. Prepared from t-butyl chloride.³ Distillation through a 12-plate column gave a product with b.p. 89°C./42 mm.; m.p. 35°C.

¹Brown, J. Am. Chem. Soc., **60**, 1325 (1938).

²Gilman and Blatt, "Organic Syntheses," John Wiley and Sons, New York City, 1941, Coll. Vol. I, p. 263.

³Loc. cit., p. 524.

Butyric anhydride. Distillation of Eastman's pure product through a 12-plate column gave a product with b.p. $86^{\circ}\text{C.}/12\text{ mm.}$

Acetophenone. Distillation of Eastman's pure material through a 10-plate column gave a product with b.p. $52^{\circ}\text{C.}/2\text{ mm.}; n_{\text{D}}^{20} = 1.5341.$

Propiophenone. Prepared from propionic anhydride (Eastman's) and benzene.⁴ Distillation of the material thus obtained through a 100-plate Podbielniak column gave a product with b.p. $83^{\circ}\text{C.}/5\text{ mm.}; n_{\text{D}}^{20} = 1.5250.$

Phenyl isopropyl ketone. Prepared from isobutyryl chloride and benzene.⁴ Distillation of the material thus obtained through a 20-plate column packed with glass helices gave a product with b.p. $100-2^{\circ}\text{C.}/13\text{ mm.}; n_{\text{D}}^{20} = 1.5176.$

Ethylbenzene. Distillation of Eastman's material through a 10-plate column packed with glass helices gave a product with b.p. $135^{\circ}\text{C.}; n_{\text{D}}^{20} = 1.4960.$

p-Methoxy-n-propylbenzene. Prepared by reducing Eastman's pure anethole in ethyl alcohol over Raney nickel at 50 lbs. hydrogen pressure. Distillation of the material thus obtained through a 100-plate Podbielniak column gave a product with b.p. $76.5^{\circ}\text{C.}/6\text{ mm.}; n_{\text{D}}^{20} = 1.5040.$

Diacyl peroxides. The preparation of these reagents is described in full below.

The Preparation of the Peroxides. The peroxides used in the experiments hereafter described are somewhat hazardous materials to handle. General directions for the preparation of all of them are given first. These directions are followed by a statement of the precautions advisable in carrying out the individual steps.

⁴Adams and Noller, J. Am. Chem. Soc., 46, 1889-96 (1924).

The diacyl peroxides were prepared by the reaction of the appropriate acid anhydride with sodium peroxide. If the diacyl peroxide was to be decomposed in an inert solvent, it was prepared directly in that solvent and was never isolated in the pure form. (This method of preparation is to be preferred whenever feasible. Where it cannot be used, the peroxide is prepared in ether solution and the ether removed by evaporation.) The acid anhydride, dissolved in the appropriate solvent, was placed in a 3-necked flask fitted with a thermometer and a stirrer. This flask was immersed in a salt-ice bath. When the temperature of the solution had dropped to $-10^{\circ}\text{C}.$, the sodium peroxide (1 mole of sodium peroxide per 2 moles of anhydride) was slowly added over a 15-30 minute period. During this addition, the temperature of the solution was kept below $0^{\circ}\text{C}.$ by efficient cooling and constant stirring. After the addition was complete, the mixture was stirred for one hour at the same temperature. After this period, water was added from a medicine dropper, beginning with one drop at a time, and gradually increasing the number of drops until finally about 0.5 cc. of water could be added without causing an appreciable rise in the temperature of the mixture. Beyond this point, the water was added dropwise (very slowly) from a small dropping funnel until the white semi-solid mass in the flask was completely dissolved. At this point the reaction mixture consisted of an aqueous and a non-aqueous layer. The non-aqueous layer was separated and dried first over calcium chloride and finally over drierite. Where any solvent other than ether was used, the solution thus obtained was used directly in the decomposition reactions. Where ether was used, the procedure for obtaining the pure diacyl peroxide varied with the anhydride employed.

The pure diacetyl peroxide was obtained from ether solution as follows. The dried solution was placed in a round-bottom flask and left overnight at -80°C . The ether was then carefully decanted from the white crystals deposited at that temperature, and the flask containing the crystals was evacuated at room temperature until a constant pressure of 1 mm. or less was obtained. Air was then very slowly admitted into the system through a capillary tube (the shock due to a sudden back-rush of air at this point causes the peroxide to explode). The peroxide was washed rapidly in the flask with 100 cc. of dry, cold carbon tetrachloride which was then immediately decanted. The evacuation was repeated as before and air again carefully admitted. Finally the peroxide was weighed and dissolved in the desired solvent.

Pure dibutyryl peroxide was obtained from an ether solution as follows. The dried solution was placed in a round-bottom flask kept at 0°C . The flask (connected through a calcium chloride tube) was evacuated first with a water pump and finally with an oil pump. The dibutyryl peroxide thus obtained was weighed and dissolved in the solvent in which it was subsequently to be decomposed.

It is important to remove all traces of ether from these peroxides because of the tendency of free radicals to attack ether even when it is present in low concentrations. The solutions of the peroxides were titrated for peroxide content⁵ just before they were used in the decomposition reactions. Such titrations showed that the peroxides prepared in this way were 96-99% pure.

The peroxides used in this work are already reported in the literature,⁶ but the experience gained in handling these

⁵Kokatnur and Jelling, J. Am. Chem. Soc., 63, 1432 (1941).

⁶Gambarjan, Ber., 42, 4010 (1907).

compounds is worth recording here. Repeated experiments have revealed that, although these diacyl peroxides are relatively unstable, they are prepared with less hazard from acid anhydrides than from acid chlorides.* Diacetyl peroxide, the most sensitive of them all, has been known to develop minor explosions accompanied by fire within the reaction vessel during its preparation. This is particularly likely to occur if the sodium peroxide contains small lumps. Any such lumps in the commercial powder should be removed before this powder is added to the reaction mixture. When ether is used as the solvent, too rapid stirring of the reaction mixture is dangerous because, under these conditions, sodium peroxide granules are thrown on the sides of the flask and left high and dry when the ether evaporates. Then during the addition of water, sufficient heat may be evolved about these crystals clinging to the sides of the flask to ignite the ether. When this occurs, there is serious danger that both the ether and the peroxide may explode. Elbow-shaped stirrers are not desirable for this work; Herschberg-type or moon-shaped stirrers are preferable. Slow, but efficient, stirring is a highly desirable safety precaution. Dry solid diacetyl peroxide is extremely sensitive to both heat and shock. It must never be removed in the solid form from the vessel in which it is prepared. In solution it is relatively safe to handle.

The Decomposition Reactions. The decompositions of the diacyl peroxides were carried out in a round-bottom flask equipped with a condenser and a capillary tube leading almost to the bottom of the flask. The 18-inch reflux condenser was connected to a train of three traps immersed in methyl-alcohol-dry-ice baths

*See footnote on page 53.

followed in succession by three large U-tubes filled with soda-lime, and one U-tube filled with ascarite. Beyond these absorbers was a calcium chloride tube leading directly to an apparatus in which the inert gases which escaped absorption in the train were collected over water. Whenever chlorine atoms were present in the molecules of the solvent, a U-tube filled with a mixture of glass wool and Michler's ketone was interposed between the last cold trap and the first soda-lime tube in order to catch any hydrogen chloride which might be formed in the reaction.

In most of the decomposition reactions, carbon dioxide, methane, and methyl acetate were the only volatile products formed. The procedure used when these were the only volatile products will be described in detail. In the other reports of experiments in which volatile products other than those mentioned were formed, the variations from the standard procedure will be noted.

A titrated solution of the diacyl peroxide was slowly introduced (through the capillary) beneath the surface of a heated portion of the same solvent. The molar ratio of the total amount of solvent used to diacyl peroxide should be at least ten to one. As soon as the peroxide entered the heated solvent there was a copious evolution of gases. At the temperature at which the reaction was run the carbon dioxide and methane carried over with them the methyl acetate which is formed. The methyl acetate was caught in the cold traps. The carbon dioxide was absorbed in the soda-lime and ascarite tubes (weighed beforehand). The methane passed through these tubes and was collected at the end of the system.

The experiments were run on such a scale that the volume of methane collected was large (8 to 20 liters). It was therefore inconvenient to collect and analyze all of this gas. The gas

collector was therefore equipped with a three-way stopcock through which samples of gas were at intervals withdrawn before they reached the final collecting vessel. These combined samples (about 1 liter) were analyzed (Regnault molecular weight determination).

When all the peroxide solution had been added and the gas evolution had ceased the total volume of methane produced was measured. Then a stream of dry nitrogen was passed through the capillary tube. This gas (about 3 liters) bubbling through the reaction mixture swept all the carbon dioxide out of the reaction flask. At this point the reaction flask was disconnected from the train of cold traps which were stoppered at the in-flow end. Almost all of the methyl acetate was found in the first trap. The second and third traps were therefore immersed in an ice-bath ($0^{\circ}\text{C}.$) and the first was allowed to warm to room temperature. By this means the carbon dioxide dissolved in the methyl acetate was driven over into the absorption tubes, while any volatilized methyl acetate was caught in the second and third traps. The contents of all three traps were then combined and distilled through an 8-inch Vigreux column. The fraction boiling from 56.5 to $58^{\circ}\text{C}.$ was collected, weighed, and its index of refraction determined. (In one preliminary experiment the material thus collected was further identified as methyl acetate by conversion to a known solid derivative.) The amount of carbon dioxide evolved in the reaction was determined by the increase in weight of the U-tubes. The liquid remaining in the reaction flask was fractionated by methods appropriate to the particular solvent and peroxide used.

Decomposition of Diacetyl Peroxide in Various Solvents.

All the diacetyl peroxide used for these experiments was isolated

from ether solution as previously described. The various solvents were added directly to the weighed material thus obtained. Where possible, the solution thus prepared was also analyzed⁵ for its peroxide content. Through the dropping funnel and capillary tube, it was then introduced beneath the surface of the heated portion of the solvent. At the temperatures used in the work here recorded, the residual liquid left in the reaction flask after the reaction was apparently complete showed no test for peroxide. (If, however, such test should indicate the presence of peroxide at this point, it is advisable before working up the reaction products, to continue heating the reaction mixture until the test for peroxide is negative.) The first step in working up the non-volatile reaction products was to distill the mixture at reduced pressure from a modified Claisen flask through an 18-inch Vigreux column.

Solvent 1: Trichloroacetyl Chloride. Diacetyl peroxide (43.5 g., 0.369 mole) was dissolved in 150 cc. of trichloroacetyl chloride. This solution was introduced into 150 cc. of trichloroacetyl chloride heated to 110°C. In this reaction it was expected to obtain methyl chloride instead of methane. However, a considerable amount of methane was also formed. This gas was identified in the usual manner.

Methane, 7.8 liters, 0.348 mole; M. W.: obs. 16.68; calc. 16.00
Vapor pressure at -195°C.: obs. 13 mm.; Literature value 13 mm.
The amount of carbon dioxide formed was 22.44 g., 0.51 mole.
The amount of hydrogen chloride formed was 2.52 g., 0.07 mole.

The methyl chloride was caught in the first cold trap (-80°). These traps were treated in the usual fashion, but an additional trap (-80°C.) was attached at the end of the train beyond the U-tubes. When the first trap was warmed to room

temperature, the methyl chloride distilled through the U-tubes and was caught in the final trap where it was weighed. Then it was transferred to a vacuum line where its molecular weight was determined. M. W.: obs. 50.45; 50.92; calc. 50.45. The liquid remaining in the first three traps at room temperature was distilled; b.p., 52°C., $n_D^{20} = 1.3898$, (7.2 g., 0.09 mole). It was an acid chloride. It was converted to an anilide which did not depress the melting point of a known sample of acetanilide. The compound was therefore acetyl chloride. This product was probably formed by the interaction of methyl acetate with the excess trichloroacetyl chloride.

The first fraction obtained when the contents of the reaction flask were distilled was unreacted trichloroacetyl chloride. Most of the remaining material boiled at 84°C./8 mm. or 116.5°C./20 mm. It was a yellow oil difficult to hydrolyze even with dilute alkali. The following physical and chemical constants of this liquid were determined. These findings all agree with the

TABLE 4

	Observed	Calculated for $C_4O_2Cl_6$
M. W. (Cryoscopic in benzene)	306; 313	293
Saponification eq.	74.03; 74.43	73.25
Refractive index $n_D^{20} =$	1.5148; 1.5147	
% Chlorine	72.31; 72.23	72.67

assumption that the material is tetrachlorosuccinyl chloride. One portion of the tetrachlorosuccinyl chloride was converted to the di-N-methyl anilide which, after recrystallization from a 50% mixture of chloroform and ethyl alcohol, melted at 173°C. This

product when analyzed gave the following results:

% Cl	Observed:	32.98	Calc. for	$C_{18}H_{16}O_2N_2Cl_4$:	32.70
% N	"	6.63	"	"	6.45

Another portion was treated with absolute methyl alcohol with which it reacts vigorously. The product was distilled in vacuo and collected at 130-3°C./8 mm. It was a colorless liquid, $n_D^{20} = 1.4924$; 1.4926, and its analysis gave the following results.

% Cl	Observed:	50.13, 50.32	Calc. for	$C_6H_6O_4Cl_4$:	50.00
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This ester (9.5 g.) dissolved in methyl alcohol was reduced catalytically (Adam's catalyst) with hydrogen at 60°C. under 60 lbs. pressure. A fruity-smelling colorless oil (b.p. 65°C./4 mm.) was obtained. This oil had a refractive index, $n_D^{20} = 1.4204$. (Recorded value for dimethyl succinate is $n_D^{20} = 1.4200$.) The ester was converted by the method of Hardy⁷ to the di-anilide which, when recrystallized from aqueous ethyl alcohol melted at 221°C. The recorded melting point of succinilide is 223°C. A mixture of the material here obtained with authentic succinilide melted at 223°C. This evidence conclusively establishes the structure of these derivatives of tetrachlorosuccinic acid.

Solvent 2: Methyl Dichloroacetate. Diacetyl peroxide (48.7 g., 0.412 mole) was dissolved in 150.9 grams of methyl dichloroacetate. This solution was introduced into 134.5 grams of pure methyl dichloroacetate heated to 115°C. The methane and carbon dioxide were collected and identified in the usual manner.

Carbon dioxide, 29.48 g., 0.67 mole.

There was formed 11.42 liters S. C., 0.51 mole of methane.

Methane:	M. W.:	obs. 17.93	Calc. for	CH_4 :	16.00
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⁷Hardy, J. Chem. Soc., p. 398 (1936).

Hydrogen chloride (0.36 g., 0.01 mole) was also formed.

The methyl acetate (7 g., 0.10 mole) formed in this experiment was distilled from soda-lime in order to remove all traces of hydrogen chloride. The pure product thus obtained had the following constants: b.p. 56-7°C., $n_D^{20} = 1.3600$.

The first fraction obtained when the contents of the reaction flask were distilled was unreacted methyl dichloroacetate. Most of the remaining material, a clear colorless oil, boiled at 133°C./8 mm. or 103°C./2 mm. The boiling point and refractive index ($n_D^{20} = 1.4924$) of this material proved it to be dimethyl tetrachlorosuccinate, the same substance as that obtained in the previous experiment.

The small amount (5-8 g.) of residual high-boiling materials formed in this and the preceding experiment decomposed when attempts were made to distill them from a molecular still.

Solvent 3a: Dimethyl Succinate at 110°C. Diacetyl peroxide (24.5 g., 0.208 mole) was dissolved in dimethyl succinate (133 g.). This solution was introduced into dimethyl succinate (111 g.) heated to 110°C. Carbon dioxide (13.07 g., 0.297 mole), methane (5.75 liters, 0.257 mole), and methyl acetate (b.p. 59°C., $n_D^{20} = 1.3610$, 2.8 g., 0.038 mole) were collected and identified in the usual manner.

The first fraction obtained when the contents of the reaction flask were distilled was unreacted dimethyl succinate (201.3 g.; $n_D^{20} = 1.4194$). This fraction contained no unsaturated material (bromine test). Dimethyl maleate or dimethyl fumarate were therefore absent. The residue, a clear colorless glass, was dissolved in 200 cc. of ethyl ether. This ethereal solution, after standing overnight, deposited crystals. The crystalline material (0.75 g.) was removed by filtration and washed several times with

ether. This substance which, after recrystallization from methyl alcohol, melted at 134°C . was later shown to be one form of 1,2,3,4-tetracarbomethoxybutane.

Anal. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_8$: C, 49.65; H, 6.24

Found: C, 50.51; H, 6.34

Mol. wt. calc., 290. Found: 298 (Raast method)

Sap. Eq. calc., 73. Found: 68.6

This precipitated ester was converted to the tetra-amide by allowing it to stand for three weeks in a solution of methyl alcohol and ammonium hydroxide. The product, after recrystallization from water, decomposed at 303°C .

Anal. Calc. for $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4$: N, 24.34; Found: N, 24.11

The ethereal filtrate was concentrated in vacuo. The viscous residual liquid (29.3 g.) crystallized after standing for about three months in a desiccator. The solid product, when purified by recrystallization from methyl alcohol, melted at $71-3^{\circ}\text{C}$. This substance proved to be a stereoisomeric form of the 1,2,3,4-tetracarbomethoxybutane.

Anal. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_8$: C, 49.65; H, 6.24

Found: C, 49.97; H, 6.26

Mol. wt. calc., 290. Found: 299 (Raast method)

Sap. Eq. calc., 73.0. Found: 81.2

The tetra-amide of this low-melting form was prepared by treating the ester with a methyl alcohol solution of ammonium hydroxide. The product after recrystallization from water, melted with decomposition at 293°C .

Anal. Calc. for $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4$: N, 24.34; Found: N, 24.27, 24.26

Solvent 3b: Dimethyl Succinate at 160°C . Diacetyl peroxide (42.1 g., 0.355 mole) was dissolved in 140.0 grams of dimethyl succinate. This solution was introduced into dimethyl

succinate (129.8 g.) heated to 160°C. The carbon dioxide (25.56 g., 0.581 mole), methane (10.0 liters S. C., 0.446 mole; m. w. 16.84), and methyl acetate (b.p. 57°C., $n_D^{20} = 1.3610$; 5.9 g., 0.08 mole), were collected and identified in the usual manner.

The residual liquid in the reaction flask was worked up exactly as described in Experiment 3a. Unreacted dimethyl succinate (230.5 g., 1.57 moles, b.p. 65°C./4 mm.) was collected. From the material (42.5 g.) remaining after this solvent had been removed was isolated (0.8 g. of) the high-melting (134°C.) form of 1,2,3,4-tetracarboxymethoxybutane and 41.7 grams of the low-melting (73°C.) form of this ester.

Both forms of this ester were hydrolyzed by gentle warming in 6 N. hydrochloric acid to the corresponding acid. From the low-melting (73°C.) ester was obtained an acid melting at 187-9°C. The acid derived from the hydrolysis of the high-melting (134°C.) ester melted with decomposition at 220°C. Both of these parent acids as well as their respective tetramethyl esters have previously been reported in the literature.⁸

Solvent 3c: Dimethyl Succinate and Methyl Acetate. Diacetyl peroxide (41.4 g., 0.351 mole) was dissolved in a mixture of dimethyl succinate (156.0 g.) and methyl acetate (111.0 g.). This solution was introduced into a mixture of 31.0 grams of dimethyl succinate and 22.0 grams of methyl acetate heated to 110°C. The carbon dioxide (18.39 g., 0.372 mole), methane (8.17 liters S. C., 0.36 mole, m.w. 17.05), and methyl acetate (b.p. 56°C.) were collected and identified in the usual way. In this instance the methyl acetate caught in the cold trap was distilled and added to the first fraction of the distillate as follows.

⁸Auwers, Ber., 26, 364 (1893); 27, 1114-5 (1894).

When the contents of the reaction flask were distilled, the first fraction obtained was unreacted methyl acetate. This material was combined with the material caught in the cold traps during the reaction and redistilled. By this means 134.5 grams of methyl acetate (b.p. 56-7°C., $n_D^{20} = 1.3595$) was recovered. The remaining material was distilled at reduced pressure, and 141.7 grams of dimethyl succinate was reclaimed. The residue obtained by removal of these unreacted portions of the solvent was distilled from a small modified Claisen flask through a six-inch Vigreux column. The first fraction (6 g.) boiled at 80-178°C./5 mm.; the second (37.1 g.) was collected at 178-80°C./5 mm. The second fraction proved to be a mixture of the two forms of tetracarboxymethoxybutane obtained in the previous experiments. The mixture was treated as previously described, and by this means 1.2 grams of the high-melting form (m.p. 133°C.) and 35.9 grams of the low-melting (73°C.) form were obtained. The first fraction (b.p. 80-178°C./5 mm.) was examined to see whether it contained any of the tricondensate, trimethyl tricarballylate. The material was converted to amides by allowing it to stand for several days in a solution of methyl alcohol and ammonium hydroxide. Fractional crystallization of the amides thus obtained gave first a substance (m.p. 290°C. with decomposition) which proved to be the amide of the low-melting form of the tetracarboxybutane. The remaining crystals melted at 247-50°C. and did not depress the melting point (250°C.) of an authentic sample of succinamide. There was no evidence that any trimethyl tricarballylate had been formed in the reaction. These results indicate that the material under examination was a mixture of dimethyl succinate and tetracarboxymethoxybutane.

Solvent 4: Methyl Acetoacetate. Diacetyl peroxide (26.5 g., 0.224 mole), was dissolved in 96.0 g., 0.83 mole of methyl acetoacetate, and this solution* was introduced into methyl acetoacetate (34.0 g., 0.3 mole) heated to 120°C. Carbon dioxide (16.24 g., 0.369 mole), methane (6.34 liters S. C.; 0.282 mole; m.w. 16.38), and methyl acetate (4.4 g.; 0.06 mole; b.p. 56°C.; $n_D^{20} = 1.3588$) were collected and identified in the usual manner.

The first fraction obtained when the contents of the reaction flask were distilled was unreacted methyl acetoacetate (b.p. 55°C./2 mm., 98.7 g.). There remained a heavy oil (24 g.) which crystallized when allowed to stand. The crystalline mass was triturated twice with methyl alcohol, and then recrystallized from the same solvent. The white material thus obtained melted at 138-40°C. This material was proved in the following manner to be dimethyl a,a' diacetosuccinate. Treatment with a methyl alcoholic solution of ammonium hydroxide and subsequent hydrolysis gave 2,5-dimethyl pyrrole-3,4-dicarboxylic acid. The observed melting point of this acid was 247-50°C. The value recorded in the literature⁹ is 250-1°C.

Solvent 5: Ethylbenzene. Diacetyl peroxide (67 g., 0.56 mole) was dissolved in ethylbenzene (163 g., 1.54 moles), and this solution was introduced into 84.0 g., 0.79 mole, of ethylbenzene heated to 125°C. Carbon dioxide (40.59 g., 0.90 mole), methane (13.65 liters S. C., 0.61 mole, m.w. 16.6), and methyl acetate (b.p. 57.5°C.; $n_D^{20} = 1.3610$, 7.1 g., 0.09 mole) were collected and identified in the usual manner.

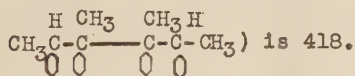
*It is not feasible to analyze this solution for its peroxide content by the method cited.

⁹Knorr, Ber., 18, 302 (1885).

The first fraction obtained when the contents of the reaction flask were distilled was unreacted ethylbenzene (b.p. 50°C./20 mm.; $n_D^{20} = 1.4950$; 179.5 g.). The residue (62.5 g.) from this distillation cooled to form a mass of needles immersed in oil.

This mixture was transferred to a fritted-glass filter on which the crystals were separated from the oil and washed with methyl alcohol. The crystals (18.5 g.) after recrystallization from methyl alcohol, melted at 123-5°C. The recorded¹⁰ melting point for meso-2,3-diphenylbutane is 126°C. The methyl alcohol solution of the oily product was distilled. After removal of the solvent, a water-white oily fraction was collected (b.p. 106°C./2 mm.; $n_D^{20} = 1.5517$; 19.4 g.; 0.09 mole). These constants agree with those recorded for racemic 2,3-diphenylbutane.¹⁰

A glassy residue (18.5 g.), which could not be crystallized, remained in the distilling flask. The molecular weight (425.) of this material was determined in a Swietoslawski¹¹ apparatus with carbon tetrachloride as the solvent. The calculated molecular weight for a tetracondensate (presumably $C_{32}H_{34}$:



Solvent 6: Isopropylbenzene. Diacetyl peroxide (52.5 g., 0.436 mole) dissolved in isopropyl benzene (146.5 g., 1.22 moles) was introduced into isopropylbenzene (95.5 g., 0.796 mole) heated to 125°C. Carbon dioxide (32.55 g., 0.74 moles), methane (12.49 liters S. C.; 0.56 mole; m.w. 16.55), and methyl acetate (b.p. 56.5°C.; $n_D^{20} = 1.3610$; 4.5 g., 0.06 mole) were collected and identified in the usual manner.

¹⁰Conant and Blatt, *J. Am. Chem. Soc.*, **50**, 555 (1928).
Klages, *Ber.*, **35**, 2639 (1902).
Ott, *Ber.*, **61**, 2139 (1928).

¹¹Swietoslawski, *J. Chem. Ed.*, **5**, 469 (1928).

The first fraction obtained when the contents of the reaction flask were distilled was unreacted isopropylbenzene (172.0 g.; 1.43 moles; $n_D^{20} = 1.4900$). The residue was a mass of white needle-like crystals which, after recrystallization from ethyl alcohol, melted at 115°C. This melting point corresponds to the recorded¹² melting point of 2,3-diphenyl 2,3-dimethylbutane. The total weight of this substance was 65.0 grams (0.27 mole). No material of higher molecular weight was present.

Solvent 7: p-Methoxy-n-propylbenzene. Diacetyl peroxide (59.8 g.; 0.506 mole) was dissolved in p-methoxy-n-propylbenzene (186 g., 1.24 moles), and this solution was introduced into p-methoxy-n-propylbenzene (204.5 g., 1.36 moles) heated to 145°C. Carbon dioxide (32.79 g., 0.745 mole), methane (12.89 liters S. C., 0.57 mole; m.w. 17.1), and methyl acetate (4.0 g., 0.05 mole; b.p. 56°C.; $n_D^{20} = 1.3594$) were collected and identified in the usual manner.

The first fraction obtained when the contents of the reaction flask were distilled was unreacted p-methoxy-n-propylbenzene (325.0 g., 2.17 moles; b.p. 62-5°C./3 mm.; $n_D^{20} = 1.5032$). The residue (69.0 g.) from this distillation cooled to form a mass of pale yellow crystals immersed in an oil. The crystals (22.5 g.) were collected on a fritted-glass disc and recrystallized from ethyl alcohol. They melted at 142°C. The recorded¹³ melting point for the higher-melting (meso) form of hexestrol dimethyl ether is 146°C. The oil (45.0 g.) was fractionated from a small modified Claisen flask with 6-inch Vigreux column. The first fraction, a water-white liquid, boiled at 172-5°C./2 mm. ($n_D^{20} =$

¹²Klages, Ber., 35, 2638 (1902).

¹³Docken and Spielman, J. Am. Chem. Soc., 62, 2163 (1940).

1.5455; 21.5 g.). This material is undoubtedly the racemic form of hexestrol dimethyl ether previously reported.¹³

A higher boiling material (12.0 g.) remained in the distilling flask. The average molecular weight¹¹ of this material was 460. This value is close to that (446) calculated for a tri-condensate, $C_{30}H_{38}O_3$.

Solvent 8: Trimethyl Acetic Acid. Trimethyl acetic acid (211.5 g., m.p. 35°C.), heated just to its melting point was carefully poured onto crystalline diacetyl peroxide (61.5 g., 0.52 mole). The peroxide dissolved completely, and the solution remained liquid at room temperature. This solution was introduced into trimethyl acetic acid (146.7 g.) heated to 125°C. Carbon dioxide (38.95 g., 0.88 mole), methane (13.55 liters S. C., 0.60 mole; m.w. 16.53), and methyl acetate (6.0 g., 0.08 mole; b.p. 56.5°C.) were collected and identified in the usual manner.

The first fraction obtained (after four grams of acetic acid were collected) when the contents of the reaction flask were distilled was unreacted trimethyl acetic acid (313 g., 3.06 moles, b.p. 56°C./5 mm.). The residue (44.0 g.) crystallized in the distilling flask. These crystals after recrystallization from aqueous ethyl alcohol melted at 186-7°C. (unc.). This melting point agrees with the recorded¹⁴ melting point for a,a,a',a'-tetramethyl adipic acid. The mother liquor from this recrystallization contained a small amount (3-4 g.) of a high-boiling syrup which could not be crystallized.

Solvent 9a: Methyl Ethyl Ketone. Diacetyl peroxide (61.0 g., 0.516 mole) was dissolved in methyl ethyl ketone (129. g., 1.79 moles), and this solution was introduced into methyl

¹⁴Farmer and Kracovski, J. Chem. Soc., 2318-23 (1926)

ethyl ketone (159. g., 2.21 moles) heated to 78°C. Carbon dioxide (34.76 g., 0.79 mole), methane (14.00 liters S. C., 0.62 mole; m.w. 16.95), and methyl acetate (6.0 g., 0.08 mole; b.p. 56-7°C.) were collected and identified in the usual manner.

The first fraction obtained when the contents of the reaction flask were distilled was unreacted methyl ethyl ketone (237 g., 3.30 moles; b.p. 78.5°C.; $n_D^{20} = 1.3800$). The second fraction was collected at 57°C./1 mm. (38.3 g.). This oil was refractionated through a 10-plate column and boiled at 92°C./30 mm.; $n_D^{20} = 1.4330$.

Calc. for $C_8H_{14}O_2$: C, 67.60 H, 9.86

Found: C, 67.44 H, 9.56

This product gave positive ferric-chloride and iodoform tests. It colored the skin red. These reactions suggested the material was the expected 3,4-dimethyl hexane 2,5-dione:

$CH_3CO-CHCH_3CHCH_3-COCH_3$. This structure was proved as follows.

When oxidized with sodium hypobromite the material gave an almost quantitative yield of α,α' -dimethyl succinic acid (meso and racemic forms). The melting point of the meso form of the acid thus obtained was 205-6°C. The recorded melting point is 209°C. Treatment of the diketone with ammonium hydroxide in methyl alcohol yielded the known 2,3,4,5-tetramethyl pyrrole. When recrystallized from methyl alcohol this pyrrole melted at 109-110°C. The recorded¹⁵ melting point is 110°C. The diketone when treated with phenyl hydrazine in ethyl alcohol gave the known pyridazine derivative which melted at 127-8°C. The recorded¹⁵ melting point for this derivative is 130°C.

¹⁵Ciamician, Ber., 45, 1542 (1912).

Demetre-Vladesco, Bull. Soc. Chim. (Paris), (3), 6, 809 (1891).

Anal. Calc. for $C_{14}H_{18}N_2$: N, 13.0

Found: N, 12.6

After the diketone had been distilled there remained a heavier oil (4.3 g.) which decomposed when attempts were made to distill it at 1 mm.

Solvents 9b, 9c, 9d: Acetophenone, Propiophenone, and Phenyl Isopropyl Ketone. Diacetyl peroxide was decomposed in acetophenone, propiophenone, and phenyl isopropyl ketone in the same manner already described for various other solvents. Carbon dioxide, methane, and methyl acetate were collected and identified. The yield of methane, however, was in all three cases unexpectedly low, about one half of the amount which would be predicted on the basis of the reactions previously described. From the resinous materials remaining after removal of the unreacted solvents in these cases no definite products have been isolated.

The Decomposition of Dibutyryl Peroxide in Isopropylbenzene. Dibutyryl peroxide (0.464 mole) was prepared from butyric anhydride* by the method described above using isopropylbenzene as the solvent. This solution after being successively dried over calcium chloride and drierite at 0°C . was analyzed⁵ for peroxide content and added dropwise beneath the surface of more cumene held at 125°C . The same system of traps and absorption train was employed as described above but here the traps were immersed in baths at 0°C . Carbon dioxide (32.4 g., 0.73 mole) was absorbed in the soda-lime tubes, while the inert volatile gases (10.88 liters, 0.49 mole) were collected over water. Analysis of this

*The use of the acid chlorides for the preparation of these peroxide has often resulted in effervescence approaching explosive violence, while with the anhydrides the reactions seem to proceed smoothly and without hazard. It is thought that the possible generation of chlorine atoms might be the source of this violence.

gaseous product gave the following data:¹⁶

M. W. before unsaturates removed---43.1

M. W. after unsaturates removed----44.1

M. W. calculated for C_3H_8 -----44.0

Percent unsaturation-----10.0% (propylene)

Percent saturated-----90. % (propane)

The material in the reaction vessel was distilled in vacuo and the unreacted solvent, isopropylbenzene (420. g., 3.5 moles) was reclaimed at 63.5°C./38 mm., $n_D^{20} = 1.4940$. Remaining in the vessel after the solvent was completely removed was a white crystalline product (45.5 g.; 0.19 mole; 78.3% yield), 2,3-diphenyl 2,3-dimethylbutane which after recrystallization from ethyl alcohol melted at 115°C. M.p. of the mixture of this product and a known sample of 2,3-diphenyl 2,3-dimethylbutane was 115°C.

The Decomposition of Ditrimethyl Acetyl Peroxide in Isopropylbenzene. Ditrimethyl acetyl peroxide (0.2 mole) was prepared in the manner described above, using cumene as the solvent, and the solution of the peroxide was dried over calcium chloride kept at 0°C. This solution was then added dropwise beneath the surface of isopropylbenzene held at 135°C. in a flask to which was attached a condenser and the same system of traps and absorption tubes as described above, here again the traps were immersed in baths at 0°C. Carbon dioxide (11.1 g.; 0.25 mole) was absorbed in the soda-lime tubes, and a gas (7.2 liters S. C., 0.28 mole) was collected in the gas chamber at end of system. Molecular weight determination of this gas gave a value, 56.92 (m.w. calculated for isobutane-58.08, for isobutene-56.08). Determination of the percentage of unsaturation by method of Kharasch, Lewis,

¹⁶Kharasch, Lewis, and Reynolds, J. Am. Chem. Soc., 65 493 (1943).

and Reynolds¹⁶ gave anomalous results. The percentage of unsaturation was determined by condensing a weighed sample of the gas into a tube containing a known volume of standard bromate-bromide¹⁷ solution and equipped with a side arm with stopcock for introducing hydrochloric acid. After introduction of acid the tube was sealed off in vacuo and the contents allowed to warm up to room temperature. After standing overnight an excess of potassium iodide solution was added, and the free iodine liberated by the unreacted bromine was back-titrated with standard thiosulfate solution. This method of analysis showed the gas to be 42% unsaturated.

In the traps kept at 0°C. there was, beside cumene, a liquid (1.5 g.) whose molecular weight was found to be 103. Vacuum distillation of the material in the reaction vessel revealed that no dimer was formed. There was left after all unreacted isopropylbenzene was removed only the small hold-up with slight decomposition from prolonged heating.

Decomposition of Dibutyl Peroxide in Trimethylacetic Acid. Dibutyl peroxide (61.0 g., 0.35 mole) was prepared in dry ether as described above. After removing the ether in vacuo at 0°C., the peroxide was dissolved in 76.5 g., 0.75 mole, of trimethyl acetic acid (warmed up to 36°C.); and this solution was added dropwise beneath the surface of trimethyl acetic acid (71.5 g., 0.7 mole) held at 135°C. in the usual apparatus while keeping the traps at 0°C. Carbon dioxide (25.63 g., 0.58 mole) was absorbed in the soda-lime tubes. In the gas chamber at the end of system was collected over water 5.08 liters S. C., 0.226 mole, of gas, the analysis¹⁶ of which gave the following data.

¹⁷Furman, "Scott's Standard Methods of Analysis," D. Van Nostrand Co., New York City, 1939, p. 2253.

M. W. before unsaturates removed----44.3
 M. W. after unsaturates removed-----45.5
 M. W. calculated for propane-----44.0
 Percentage saturation-----81.2
 Percentage unsaturation-----18.8

Collected in the traps at 0°C. was 7.5 grams (0.11 mole) of a liquid which was insoluble in cold concentrated sulfuric acid and did not decolorize bromine. Further examination of this liquid gave the following data:

TABLE 5

	Observed constants for this liquid	Literature constants for n-hexane
b.p.	67.5°C.	67.8°C.
n_D^{20}	1.3743	1.3750
M.W.	88.3	86.0

This substance (0.11) mole, being n-hexane, is equivalent to 0.22 mole of propane and represents then 50% of the total yield of gases. Also 18.8% of the 0.226 mole of gas (propane and propylene) represents only 10% of the total (0.44 mole) propyl free radicals generated (see Table 3). The ten percent (10%) unsaturation represents 20% disproportionation.

The residue in the reaction vessel was distilled in vacuo whereby the unreacted solvent was removed. From this solvent was obtained by careful fractionation at atmospheric pressure 1.0 gram of an ester boiling at 142°C., $n_D^{20} = 1.3964$. Saponification and subsequent preparation of the p-bromophenacyl ester of the acidic fragment revealed the acid to be n-butyric acid. M.p. of p-bromophenacyl ester was found to be 63-4°C. Remaining in the

flask after the first rapid distillation of the solvent was 6 grams of a residue which upon extraction with alkali yielded an acidic fraction which fails completely to crystallize on standing.

SUMMARY AND CONCLUSIONS

1. The free methyl radical, generated in solution by the thermal decomposition of diacetyl peroxide, combines with a univalent atom from the molecules of trichloroacetyl chloride, trimethyl acetic acid, methyl ethyl ketone, a series of methyl esters, some hydrocarbons, and p-methoxy-n-propylbenzene. The new free radicals thus formed dimerize. Some of the resulting dimers are not readily accessible by the older methods of syntheses.

2. Much evidence has been presented to show that the free methyl radical is very highly selective in its reactions.

3. Evidence has been presented that free aliphatic radicals vary considerably in their reactivity.

4. Two factors determine the course of the reactions of free aliphatic radicals in solution: (a) the relative reactivity of the free aliphatic radical, and (b) the comparative strengths of the bonds holding the univalent atoms in the molecules of the pure or mixed solvent in which the free radical is generated.

